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SOME EXPERIMENTS WITH PURE-METAL RESISTANCE STANDARDS

By James L. Thomas

ABSTRACT

National standardizing laboratories use wire-wound standards for maintaining the unit of electrical resistance. The material for these standards is usually manganin—an alloy of copper, nickel, and manganese. This alloy corrodes rather readily and in general its resistance does not remain as constant as is desired. It is believed that coils of pure metals, especially the noble metals, will be more stable in resistance and might be used to maintain the unit. Pure-metal standards have been constructed of copper, silver, tin, gold, and platinum wire, and measured at the ice point. The gold and platinum coils have been very stable in resistance. The construction, method of measurement, and results are given.

CONTENTS

I. INTRODUCTION

Until about the middle of the nineteenth century there was no widely accepted system of electrical units, and each experimenter used such units as were convenient for the work he was doing. As a result, the first standards of electrical resistance were copper or iron wires of stated dimensions. About 1860 Siemens[1] proposed as a unit the resistance at 0 C of a uniform column of mercury one meter

[1] Siemens, Phil. Mag., vol. 21, p. 25, 1861.

in length, having a cross section of one square millimeter. This "Siemens unit" had the advantage of being readily reproducible, and soon came into rather general use. In England, however, it was soon superseded by an "absolute unit" based upon measurements made in 1862 and 1863 under the direction of a committee of the British Association for the Advancement of Science.[2] This unit, known as the B.A. unit, was preserved by means of a group of coils constructed for the most part of precious-metal alloys.

Since about 1890 the place of precious-metal alloys has been taken largely by manganin, an alloy of copper, nickel, and manganese. It would seem, a priori, that the change in materials for the construction of resistance standards has proceeded in the wrong direction. The most important consideration in the choice of a material for primary standards is undoubtedly that of stability. It is to be expected that alloys will be less stable in composition, and hence in resistance, than pure metals, as they are more liable to changes in structure than are pure metals. Also, the base metals are more subject to surface action than the noble metals. There is, moreover, a little direct experimental evidence in favor of the use of pure metals.

Between 1862 and 1864 Matthiessen [3] investigated the stability of the resistance of a number of pure metals and alloys. From this investigation he concluded that, in addition to certain alloys, both gold and platinum would be satisfactory for use in the construction of resistance standards, and that silver and copper would not remain constant. On the basis of these results there were included two coils of platinum when in 1865 he constructed the standards for the preservation of the B.A. unit. These coils have remained in the possession of the British Association for the Advancement of Science and have been compared with one another and with the other B.A. coils by a number of observers. Nearly 70 years after their construction, Glazebrook and Hartshorn [4] concluded that probably there had been no change in the resistance of the platinum coils, and they used the platinum coils as a basis for discussing the stability of the remaining B.A. coils, made of alloys.

While the accuracy with which the platinum coils have been measured has been limited to a certain extent by their large temperature coefficients and method of mounting, their performance seemed to justify additional experiments with pure-metal resistance standards.

To obtain reasonably definite information concerning the stability of pure-metal standards, the resistance measurements should, if possible, be made with a precision of 1 part in 1,000,000. This requires that the temperature at which the measurements are made be reproducible to within 0.0002° C. This paper discusses the various problems involved in the design, construction, and measurement of pure-metal resistance standards. Data extending over a period of nearly 2 years are given for standards constructed of copper, silver, tin, gold, and platinum wire.

[2] Report of the Committee on Standards of Electrical Resistance; British Association Report, p. 345, 1864.
[3] A. Matthiesen, British Association Report, p. 351, 1864.
[4] Glazebrook and Hartshorn, British Association Report, p. 417, 1932.

II. SUITABLE TEMPERATURE FOR MEASUREMENT OF PURE-METAL STANDARDS

As stated above, in order to measure their resistance to 1 part in 1,000,000, the temperature at which the pure-metal standards are measured should be reproducible to within 0.0002° C, although the actual temperature need not be known. It is undoubtedly out of the question to immerse the standards in an oil bath and control and measure the temperature to anywhere near this accuracy.

In selecting a reproducible temperature for this purpose, one would probably consider first the ice point. This temperature, however, is a function of the conditions under which the ice is melted. There is a small change in the ice point with pressure, amounting to about 0.0001° C for a change in pressure of 1 centimeter of mercury. The ice point also depends upon the kinds and amounts of dissolved gases, the difference in the ice point for saturated and air-free ice being about 0.002° C.[5] However, it would be expected that a temperature variation of much less than 0.002° C would result from variations in the amount of dissolved air, as saturation probably takes place very rapidly and a reproducible condition is probably soon reached.

In 1927, Michels and Coeterier [6] investigated the triple point of water and suggested its use as a fixed point on the temperature scale instead of the usual ice point. Their investigation was conducted by means of a resistance thermometer and the triple point was found to be reproducible to better than 0.001° C. A more careful investigation was made by Moser [7] in 1929 at the Physikalisch-Technische Reichsanstalt, also using a resistance-thermometer method, and he reported the temperature to be reproducible to about 0.00005° C. This was probably the limit of accuracy of his determinations.

Moser's work showed that the triple point of water was suitable as a temperature at which to measure pure-metal resistance standards within 1 part in 1,000,000. However, for the present work, it was decided first to investigate the stability of pure-metal resistance standards when measured at the ice point. If they showed sufficient promise, arrangements would be made to compare the temperature of the different ice baths with that of the triple point.

III. CONTAINER FOR PURE-METAL COILS

Since the containers for the pure-metal coils were to be immersed in an ice bath, provision had to be made to prevent the bath from electrically short-circuiting the leads connecting to the ends of the resistance coils. Also it was necessary to select containers through which the heat developed by the test current would be very readily conducted to the ice bath. For the latter reason it did not seem possible to seal the coils in glass containers.

It was decided to make the containers of two thin coaxial brass tubes, practically the same as those described in Bureau of Standards Journal of Research, volume 5, page 295, 1930. The only essential change was to braze small conduits to the inner walls of the container,

[5] Foote and Leopold, Amer. Jour. Sci., vol. 11, p. 42, 1926.
[6] Michels and Coeterier, Proc. K. Ak. v. Wetensch. Amsterdam, vol. 30, p. 1017, 1927.
[7] Moser, Annalen der Physik, vol. 393, p. 341, 1929.

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around the holes through which are brought the current and potential leads. These conduits extend several inches out of the double-walled container, and the hard-rubber terminal blocks are mounted on the end of these tubes instead of being attached to the double-walled containers. The leads are insulated from each other and from the surrounding brass conduits through which they pass up to binding posts on the terminal block. A cross section of the container is shown in figure 1.

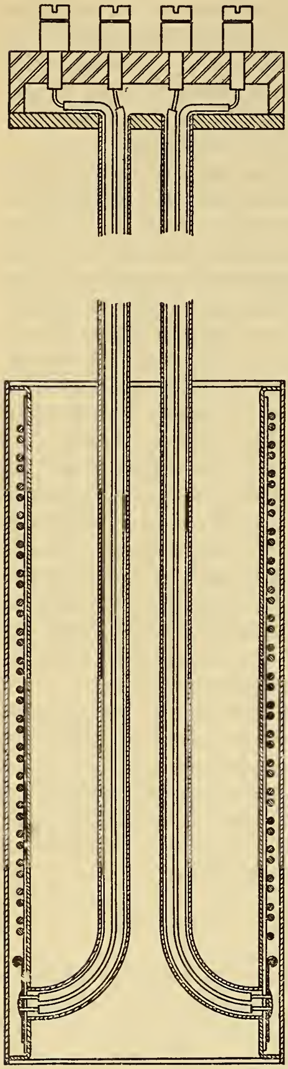

Figure 1.—*Cross section of pure-metal resistance standard.*

The double-walled container is about 2 inches in diameter and 5 inches in length. The terminal block is over 6 inches above the double-walled container. A narrow brass strip (not shown) braces the conduits at the top of the container.

The double-walled part is slightly over 2 inches (5 cm) in diameter and about 5 inches (13 cm) long. The over-all length of the standards is about 12 inches (30 cm). This allows the standards to be inserted in the ice bath contained in a wide-mouth thermos bottle, with the terminal block remaining above the thermos bottle. The conduits are in contact with the ice for a considerable length, so it is not probable that a sufficient amount of heat is conducted down along them, or through the leads, to appreciably affect the resistance.

As the pure-metal coils are very soft after annealing, it is almost impossible to anneal them on a mandrel and transfer them to the containers, as was done in the case of manganin coils. For this reason the inner tubes are insulated with a layer of mica about 0.001 inch (0.025 mm) thick, upon which the wires are wound, using a lathe to space them properly. Since the mica is not damaged by being heated to 600 C, the inner tube with the coil and insulation may be inserted in a furnace and annealed at any temperature less than that. Such was the procedure in the case of copper, gold, silver, and tin. Platinum, however, required a higher annealing temperature than the mica will withstand, so it was wound and annealed on a porcelain tube of the same diameter as the inner tube of the container. Because of its comparatively high resistivity, large enough wire could be used for a 1-ohm coil to be self-supporting, and the annealed platinum coil was readily transferred to the container.

After the coils were annealed, silk or linen thread was wound between turns of the wire. Not only does this insulate adjacent turns, but it holds the coils snugly in place so that there is no tendency for the wire to slip if the containers are turned upside down. This

type of support holds the winding without exerting much pressure against the wire itself. It also holds down the mica so that it does not tend to open outward and press against the wire.

The closed spaces in the containers were filled with air dried with calcium chloride to prevent condensation of moisture when inserted in ice. In the case of the conduits, this was found to be unnecessary. These tubes were closed by packing cotton in the top of the tubes. The small amount of dew that forms evidently spreads over the brass tubes, and the insulation resistance remains sufficiently high. The containers do not remain in ice for a very long time, so little additional moisture diffuses through the cotton.

The first pure-metal standards constructed had 10-ohm coils, and they were mounted in smaller containers than those just described. The wire for these 10-ohm coils, however, was so small that it was difficult to space the turns after they were annealed. The necessary handling of the wire partly offset the advantages of annealing the wire, and the 10-ohm standards have been abandoned.

IV. DETAILS OF RESISTANCE MEASUREMENTS

1. PREPARATION OF THE ICE BATH

Considerable care was taken in the preparation of the ice baths in order to reproduce the temperature accurately. Commercial ice was used, but care was taken to use only the clear part of the ice, avoiding the white core into which the impurities tend to collect. It is believed that such ice is as pure as ice prepared on a small scale from distilled water. One sample of this ice was melted and the water found to have a conductivity of about 3×10^{-6} ohm^{-1}–cm^{-1}. The ice was carefully shaved and then packed in a thermos bottle. A soft mush was produced by pouring distilled water into the ice. A considerable amount of water was used in order to obtain a good thermal connection between the ice bath and the walls of the resistance standard. Of course, it is necessary to pack in enough of the ice so that it does not float on top of the water.

Apparently the bath is always saturated with air, and water when added is saturated very quickly by air trapped in the finely shaved ice. No change in the temperature obtained was observed when the distilled water was boiled (to drive out the air) and immediately poured into the ice. This rapid saturation probably accounts for the accuracy with which the ice point is reproduced.

Since the ice-point temperature is a function of the pressure, the temperature obtained from the ice bath depends upon the depth of immersion. This change of temperature with depth is about 0.0001° C for 6 inches in depth. As the containers are inserted to the same depth within an inch or two, this variation in temperature is negligible.

2. HEATING BY TEST CURRENT

The inner walls of the containers are made of brass about 0.015 inch (0.375 mm) thick, and as has been stated, the insulation between

it and the coil is mica 0.001 inch (0.025 mm) thick. This construction allows a ready transfer of the heat generated in the coil by the test current. With the test current which was actually used the temperature of the coils was raised about 0.0002° C above the temperature of the ice baths in which they were measured.

3. BRIDGE FOR THE RESISTANCE MEASUREMENTS

The resistance measurements have been made by a substitution method, using a special Thompson double bridge designed and built at this Bureau. With this bridge 1-ohm standards are regularly compared to 1 part in 1,000,000, and a precision of 1 or 2 parts in 10,000,000 is attainable with standards having very low temperature coefficients.

V. DATA ON NEW STANDARDS

Table 1 shows the performance of a number of 1-ohm standards made of pure metal. The resistances given are those which would have been obtained with a negligible test current. These were obtained by making measurements with two different test currents and calculating the value for a negligible test current on the assumption that the increase in resistance of the coils is proportional to the power dissipated in them.

The resistances given in this table are expressed in terms of the Washington unit as maintained at this Bureau since 1910 by means of a group of ten 1-ohm manganin standards. These standards are intercompared every 6 months, and between intercomparisons the pure-metal standards are measured in terms of members of the group of 10. No standard with which the pure-metal coils have been compared has changed more than 1 part in 1,000,000 with reference to the mean, at successive intercomparisons of the reference group.

TABLE 1.—*Data on new standards*

1-OHM STANDARD No. 1

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1931		1932		
Nov. 23	0.999666	Mar. 24	0.999669	Material: No. 22 AWG 0.0253 inch (0.64 mm) commercial copper wire.
Nov. 24	.999666	Apr. 6	.999671	Annealing: Annealed Nov. 18, 1931, at 440 C in a large evacuated pyrex tube. About 2 hours were required to raise the temperature to 440 C, after which the heating was cut off. The tube was evacuated by keeping a vacuum pump in continuous operation.
Nov. 30	.999667	Apr. 25	.999670	
Dec. 7	.999666	Apr. 26	.999670	
Dec. 16	.999666	Apr. 27	.999670	
Dec. 31	.999667	Apr. 28	.999671	
		May 3	.999672	
1932		Aug. 22	.999680	
		Sept. 22	.999683	
Jan. 8	.999669	Oct. 19	.999683	
Jan. 19	.999667	Dec. 22	.999680	
Feb. 11	.999667			
Feb. 16	.999666	1933		
Feb. 29	.999670			
Mar. 8	.999669	May 17	.999680	
Mar. 15	.999669	Oct. 10	.999690	

TABLE 1.—*Data on new standards*—Continued

1-OHM STANDARD No. 2

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1932		1932		
Jan. 19	1.001053	Oct. 19	0.996477	Material: No. 17 AWG 0.045 inch (1.15 mm) commercial tin wire.
Jan. 26	1.000740			Annealing: annealed for a short time at 200 C in same furnace as standard no. 1.
Feb. 11	1.000387	1933		
Mar. 24	1.000185			
May 3	.999537	May 17	.9948	

1-OHM STANDARD No. 3

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1932		1932		
Jan. 8	0.998452			Material: No. 22 AWG 0.0253 inch (0.64 mm) commercial "fine" silver wire. As received the wire was very dirty and apparently had not been carefully drawn.
Jan. 19	.998483	Oct. 19	0.998702	Annealing: annealed as nearly as possible like standard no. 1.
Jan. 26	.998504			
Feb. 11	.998533	1933		
Mar. 24	.998511			
May 3	.998524	May 17	.998707	
		Oct. 10	.998913	

1-OHM STANDARD NO. 4

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1932		1932		
Jan. 19	0.999475	May 3	0.999427	Material: Same as standard no. 3.
Jan. 26	.999468	Oct. 19	.999411	Annealing: Annealed Jan. 12, 1932, in same way as standard no. 1. At end of this annealing the furnace was found to have been leaking, so furnace was again evacuated and coil raised to 500 C, at which temperature it remained for 1 hour.
Feb. 11	.999480			
Feb. 29	.999453	1933		
Mar. 24	.999427			
		May 17	.999393	
		Oct. 10	.999385	

1-OHM STANDARD NO. 5

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1932		1932		
Feb. 11	0.999481	Oct. 19	.999484	Material: Made of 0.048 inch (1.2 mm) commercial platinum wire.
Feb. 16	.999480	Nov. 23	.999484	Annealing: Before winding on porcelain mandrel, the wire was heated for a short time in air at about 1,500 C, by passing a current through it. After winding on the mandrel, it was heated in air for 36 hours at about 1,000 C.
Feb. 29	.999480	Dec. 10	.999483	
Mar. 8	.999481	Dec. 22	.999481	
Mar. 15	.999480			
Mar. 24	.999480	1933		
Apr. 6	.999481			
Apr. 19	.999481	Feb. 11	.999484	
Apr. 25	.999481	Mar. 1	.999483	
Apr. 27	.999481	May 17	.999481	
Apr. 29	.999481	Aug. 2	.999485	
Apr. 30	.999481	Oct. 10	.999483	
May 3	.999481			
Aug. 22	.999482			
Sept. 22	.999484			

1-OHM STANDARD NO. 6

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1932		1933		
Feb. 16	0.999816	Feb. 11	.999809	Material: Made of "fine" gold wire 0.0285 inch (0.724 mm) in diameter.
Feb. 29	.999812	Mar. 1	.999809	Annealing: Before winding on container tube, the wire was heated in air for a short time at 800 C. After winding on tube, it was annealed just like standard no. 1 except that furnace was heated to 500 C.
Mar. 8	.999813	May 17	.999807	
Mar. 15	.999809	Aug. 2	.999809	
Mar. 24	.999806	Oct. 10	.999806	
May 3	.999809			
Aug. 22	.999810			
Sept. 22	.999809			
Oct. 19	.999809			
Nov. 23	.999807			
Dec. 21	.999808			

VI. DISCUSSION OF DATA

1. MATERIAL

No analysis has been made of the wires used in the construction of the pure-metal coils. However, some general information has been obtained by measurements of their temperature coefficients of resistance. The average temperature coefficient, per degree C, between 0 and 25 C, in terms of the resistance at 0 C is given by α_0 in table 2.

TABLE 2.—*Temperature coefficients of resistance*

Coil no.	Material	α_0
1	Copper	0.0043
4	Silver	.0040
5	Platinum	.0032
6	Gold	.0032

These temperature coefficients show the copper and silver wires to be of high purity. The platinum and gold coils, however, must contain a considerable amount of impurities as their coefficients are below the values generally accepted for these pure metals.

2. ANNEALING

Coil no. 1 (copper) was annealed at a temperature chosen on the basis of results obtained by Bardwell.[8] He annealed a number of samples of copper wire from the same ingot at different temperatures and then measured their electrical conductivities. He found that the conductivity increased 2 or 3 percent for an annealing temperature of about 350 C. Lower temperatures produced little change in conductivity and higher temperatures gave no appreciable additional change even up to a temperature of about 700 C. Above this temperature the conductivity decreased at an accelerating rate, probably from oxidation, as the material was annealed in air.

In annealing the platinum coil (no. 5), an attempt was made to restore the crystals broken in drawing and winding without producing a larger grain size. For this reason the final annealing temperature was limited to 1,000 C.

No information was found as to the proper annealing temperatures for gold and silver. The temperatures chosen, however, seemed to leave the wire "dead soft." The temperature at which the tin was annealed was probably such as to produce a large grain size. The rapid decrease in the resistance of this coil seems to show that crystal growth is continuing at room temperature.

3. STABILITY

The pure-metal standards have not been under observation for a time long enough to warrant very definite conclusions as to their performance. However, since standards made of alloys change most rapidly in resistance during the first few months after they are completed, it is possible that the pure-metal standards will do the same. Hence, if we can produce pure-metal standards that are very stable when new, they will possibly remain so over long periods of time.

[8] Bardwell, Trans. A.I.M.E., vol. 49, p. 753, 1914.

In considering the stability of these pure-metal resistance standards, it must be kept in mind that there are several possible causes for changes in the value obtained for their resistance. That is to say, changes in the resistance as measured at the ice point may be due to differences in ice-bath temperatures, uncertainties in the electrical measurements, changes in the resistance of the manganin standards with which the pure-metal coils are compared, or actual changes in the resistance of the pure-metal coils themselves. The uncertainty of the electrical measurements is about 1 part in 1,000,000. No relative values, however, may be assigned to the other factors. Over short periods of time it would be expected that fluctuations would be due primarily to changes in ice-bath temperatures while over long periods of time changes in the resistance of the pure metal or the reference coils might be appreciable.

In the period of about 20 months since the last of these coils was completed the copper coil has apparently increased in resistance by about 25 parts in 1,000,000, the gold coil has decreased by about 10 parts in 1,000,000, the platinum coil shows little change, and the performance of the other three coils has been unsatisfactory.

The change in resistance of the gold coil occurred almost entirely during the first month, with no appreciable subsequent change. The major part of the changes in the copper, the silver, and the tin coils occurred during the hot summer months. This has also been observed in the case of sealed manganin coils, which seem to change much more rapidly in resistance during the summer months than during the winter. This is rather surprising as the difference in absolute temperature between summer and winter is not very large, and the fluctuations in temperature are probably as great during the winter months as during the summer.

Except for the change in the gold coil during the first month after its completion, both the gold and the platinum coils have remained very constant in resistance. Their performance should justify the construction of several additional coils of the same materials, in order to see whether or not the pure-metal coils remain constant among themselves. It would seem desirable, moreover, to use materials of higher purity than was obtained for the coils already constructed.

In the spring of 1933, since some of the pure-metal standards had remained very constant in resistance, it was decided to measure the temperature of the ice baths in terms of the triple point of water. A series of 20 measurements was made, extending from March 3, 1933, to May 26, 1933. For this series of measurements nine separate ice baths were used, and the triple-point bath was melted and refrozen each time the ice bath was changed. The mean of the 20 determinations showed the ice baths to have a temperature 0.0097° C below that of the triple point of water. Only one determination differed from the mean by more than 0.0001° C. The complete data, together with a description of the methods of measurement, are given in the paper immediately following this one.

Using this value for the difference in temperature between the ice bath and the triple point the resistance of the platinum coil (no. 5) on October 10, 1933, was 0.999514 Washington unit, while the resistance of the gold coil (no. 6) was 0.999837 Washington unit, each at the triple point of water.

WASHINGTON, October 28, 1933.